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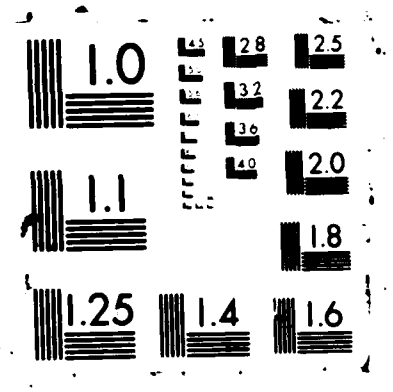
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The series of neopentylaluminum compounds, $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2H$, $Al(CH_2CMe_3)_2Br$, $(Me_3CCH_2)_2AlPPh_2$ and $(Me_3CCH_2)_2AlN(Me)H$, have been prepared by reactions typical in organoaluminum chemistry and characterized by elemental and/or group analysis, cryoscopic molecular weight measurements in benzene solution and IR and NMR spectroscopic data. All compounds in this series, except $Al(CH_2CMe_3)_3$, are associated in benzene solution. Even though the neopentyl group is considered a bulky ligand with significant steric effects, the Lewis acidity of $Al(CH_2CMe_3)_3$ has been established by the formation and characterization of adducts, $LiAl(CH_2CMe_3)_4$, $(Me_3CCH_2)_3Al\text{-}PPh_2H$ and $(Me_3CCH_2)_3Al\text{-}N(Me)H_2$. However, since $Al(CH_2CMe_3)_3$ is monomeric in benzene solution, the factors influencing the

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19. Abstract (continued)

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by

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Abstract

The series of neopentylaluminum compounds, $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2H$, $Al(CH_2CMe_3)_2Br$, $(Me_3CCH_2)_2AlPPh_2$ and $(Me_3CCH_2)_2AlN(Me)H$, have been prepared by reactions typical in organoaluminum chemistry and characterized by elemental and/or group analysis, cryoscopic molecular weight measurements in benzene solution and IR and NMR spectroscopic data. All compounds in this series, except $Al(CH_2CMe_3)_3$, are associated in benzene solution. Even though the neopentyl group is considered a bulky ligand with significant steric effects, the Lewis acidity of $Al(CH_2CMe_3)_3$ has been established by the formation and characterization of adducts, $LiAl(CH_2CMe_3)_4$, $(Me_3CCH_2)_3Al$-PPh_2H and $(Me_3CCH_2)_3Al$-$N(Me)H_2$. However, since $Al(CH_2CMe_3)_3$ is monomeric in benzene solution, the factors influencing the degree of association of organoaluminum compounds are discussed. The crystalline hydride $Al(CH_2CMe_3)_2H$ has been prepared from $Al(CH_2CMe_3)_3$ and $LiAlH_4$. The other product was LiH rather than $LiAl(CH_2CMe_3)H_3$. These observations of products are unusual in organoaluminum chemistry.

Introduction

Organoaluminum compounds[1] play important roles in chemical synthesis and catalysis as well as in the deposition of semiconducting materials by vapor phase epitaxy. Even though many organoaluminum compounds have been synthesized and fully characterized, relatively few compounds with bulky substituents have been described in detail. The new compound trismesitylaluminum[2] has been observed at room temperature to be a monomeric species in the solid state. Tris(t-butyl)aluminum[3] is also monomeric in benzene solution according to cryoscopic molecular weight measurements in benzene. In contrast, tris(trimethylsilylmethyl)aluminum[4,5] $Al(CH_2SiMe_3)_3$ has been described as a monomer-dimer equilibrium mixture in benzene solution as have the related compounds[6] $Al(CH_2SiMe_3)_2Br$ and $(Me_3SiCH_2)_2AlPPh_2$, an amphoteric ligand to transition metal carbonyl moieties[7]. The related hydride[6] $Al(CH_2SiMe_3)_2H$ represented the first organoaluminum hydride which was a crystalline solid at room temperature. Cryoscopic molecular weight measurements in benzene solution were consistent with the existence of a trimer.

As part of our continuing studies of compounds of the group 13 elements with bulky substituents, we report the syntheses and characterizations of a series of neopentylaluminum derivatives including $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2Br$, $Al(CH_2CMe_3)_2H$, $(Me_3CCH_2)_2AlPPh_2$ and $(Me_3CCH_2)_2AlN(Me)H$. The purpose of our research was to study the steric and electronic effects of the neopentyl group on the Lewis acidity and association of organoaluminum derivatives. The results of these investigations also permit direct comparisons with the corresponding trimethylsilylmethylaluminum derivatives. Even though the neopentyl and trimethylsilylmethyl groups are chemically

similar, they might have very different steric and electronic effects when bound to aluminum.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or a purified argon atmosphere. All solvents were purified before use. Aluminum(III) bromide was purified by sublimation under high vacuum at 60°C immediately prior to use. Neopentyl chloride was purchased from Fairfield Chemicals and was distilled prior to use. Neopentyllithium was prepared by reacting 12-14g of Li wire, containing 1% Na, with 80g (0.75 mol) of Me_3CCH_2Cl in 500 mL of hexane, a variation of a previously published method.[8] After ultrasonification of the reaction mixture for 48h, the resulting yellow solution was filtered from solids and then was concentrated by removing the solvent by vacuum distillation. The resulting colorless crystalline precipitate was isolated by filtration to yield 35.9g of $LiCH_2CMe_3$ (460 mmol, 61% yield based on Me_3CCH_2Cl). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Analysis for hydrolyzable neopentyl and hydride ligands were performed by acid hydrolysis and fractionation of the resulting neopentane was measured by mass and H_2 by PVT measurements. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with abbreviations w(weak), m(medium), s(strong), vs(very strong) and sh(shoulder). The Raman spectrum of $(Me_3CCH_2)_2AlN(Me)H$ was recorded on a solid sample enclosed in a sealed glass capillary by using a Spex Model 14018 spectrometer. The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical

shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ as δ 0.00 and benzene as δ 7.13. All NMR tubes were sealed under vacuum. The molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver.[9]

Synthesis of $Al(CH_2CMe_3)_3$. In a typical experiment, solid $LiCH_2CMe_3$ (9.89 g, 127 mmol) was added to a suspension of $AlBr_3$ (11.3 g, 42.4 mmol) in 100 mL of hexane at 0°C over a 20 min time period. After addition was complete, the resulting mixture was refluxed for 3 h. Then, the hexane was removed by vacuum distillation. The product, $Al(CH_2CMe_3)_3$, was then separated from LiBr by a flask to flask vacuum distillation with the flask heated to 120°C and the receiver flask cooled to -196°C. Distillation was continued for 8 h in order to ensure complete removal of product. The product was finally purified by vacuum distillation by using a short path still to yield 8.38 g (34.9 mmol), 82.3% based on $AlBr_3$. $Al(CH_2CMe_3)_3$: colorless, nonpyrophoric liquid, bp 50-52°C (static vacuum), 43-45°C (dynamic vacuum); Anal. Calcd: C, 74.92; H, 13.86. Found: C, 74.69; H, 13.94, Hydrolysis. Found: 2.98 mol CMe_4/mol $Al(CH_2CMe_3)_3$. Cryoscopic molecular weight, formula weight $Al(CH_2CMe_3)_3$ 240.46 (molality based on monomeric species, obsd mol wt, association): 0.0908, 254, 1.05; 0.0477, 225, 1.06; 0.0234, 251, 1.04. ^1H NMR (benzene) δ 1.11(s, 9.0, Me); 0.56(s, 2.0, CH_2). IR (neat liquid, cm^{-1}) 2950(s), 2860(s), 1465(s), 1358(s), 1223(s), 1120(s), 1010(s), 990(m), 925(m), 910(m), 748(s), 695(s), 675(sh), 650(sh), 465(m), 390(m), 325(m).

Synthesis of $LiAl(CH_2CMe_3)_4$. Solutions of the reagents $Al(CH_2CMe_3)_3$ (0.6587 g, 2.739 mmol) and $LiCH_2CMe_3$ (0.2139 g, 2.738 mmol) in benzene were combined at room temperature. After the reaction mixture was stirred for several hours, the solvent was removed by distillation. Then, the product

was washed with several 5 mL portions of pentane at 0°C to give 0.67 g (2.1 mmol, 78% yield of $LiAl(CH_2CMe_3)_4$ as a colorless, microcrystalline powder. $\underline{LiAl(CH_2CMe_3)_4}$: mp 184-186°C. Anal. Calcd: C, 75.40; H, 13.95. Found: C, 73.38; H, 13.54. Hydrolysis Found: 3.96 mol CMe_4/mol $LiAl(CH_2CMe_3)_4$. ^1H NMR (benzene) δ 1.18(s, 9.0, Me), 0.01(s, 2.0, CH_2). IR (Nujol mull, cm^{-1}) 2730(s), 2710(s), 1355(s), 1225(sh), 1205(s), 1135(m), 1070(m), 995(m), 925(s), 905(sh), 750(s), 670(sh), 630(s), 465(m), 405(m), 320(m).

$\underline{\text{Synthesis of } Al(CH_2CMe_3)_2Br}$. In a typical reaction, $Al(CH_2CMe_3)_3$ (0.497 g, 2.08 mmol) and $AlBr_3$ (0.277 g, 1.04 mmol), each in 15 mL of pentane, were combined in an evacuated tube and then were heated to reflux with a 60°C oil bath for 30 min. The pentane was removed and the product was purified by distillation by using a short path still to yield 0.66 g (2.6 mmol, 83% yield) of $Al(CH_2CMe_3)_2Br$. An alternative but less convenient method of purification involved recrystallization from a very small volume of pentane (1 mL per g of $Al(CH_2CMe_3)_2Br$) at -78°C. $\underline{Al(CH_2CMe_3)_2Br}$. Colorless solid, mp 58-59°C, bp 96-103°C (dynamic vacuum). Color of compound changes to tan upon trace hydrolysis. Anal. Calcd: C, 48.19; H, 8.92; Al, 10.83; Br, 32.07. Found: C, 47.36; H, 8.77; Al, 10.18; Br, 30.37. After hydrolysis Found: 1.98 mol CMe_4/mol $Al(CH_2CMe_3)_2Br$, Br, 32.1. Cryoscopic molecular weight, formula weight $Al(CH_2CMe_3)_2Br$ 249.20 (molality based on monomeric species, obsd mol wt, association): 0.133, 492, 1.97; 0.0596, 444, 1.78; 0.0310, 442, 1.77. ^1H NMR (benzene) δ 1.18(s, 9.0, Me), 0.77(s, 2.0, CH_2). IR (Nujol mull, cm^{-1}) 2860(s), 1360(s), 1230(s), 1130(s), 1095(m), 1015(m), 995(m), 930(m), 910(w), 760(s), 745(m), 670(s,br), 585(m), 465(m), 450(m), 400(w), 380(m), 335(m), 300(s).

$\underline{\text{Synthesis of } Al(CH_2CMe_3)_2H}$. A reaction vessel equipped with a Teflon high vacuum valve and a small stirring bar was charged with 3.67 g (15.3

mmol) of $Al(CH_2CMe_3)_3$, 0.640 g (16.9 mmol) of $LiAlH_4$ and 50 mL of dry heptane. The mixture was then heated with a 100°C oil bath for 5h. After cooling, the resulting suspension was filtered and the insoluble grey solid (0.52 g) was washed with the reaction solvent. The heptane was finally removed by vacuum distillation to leave 3.71 g (21.8 mmol) of $Al(CH_2CMe_3)_2H$ as a colorless, microcrystalline, heptane soluble solid. The soluble product was further purified by vacuum sublimation at 60°C for 12 h to yield 3.67 g (21.6 mmol, 95.2% yield based on $Al(CH_2CMe_3)_3$, see Results and Discussion for balanced equation) of $Al(CH_2CMe_3)_2H$. In another independent preparation of $Al(CH_2CMe_3)_2H$ (from 0.984 g of $Al(CH_2CMe_3)_3$ and 0.157 g of $LiAlH_4$), 0.0768 g of the grey heptane insoluble solid was hydrolyzed to yield 6.07 mmol of H_2. The significance of these data to the nature of the reaction products and the stoichiometry of the preparative reaction are discussed in the Results and Discussion Section.

The compound, $Al(CH_2CMe_3)_2H$, is a colorless, "wet" looking solid at room temperature and sublimes between 40 and 80°C under high vacuum. The melting point of the compound depends on its history. Samples which were obtained by sublimation at 50-60°C softened above 50°C and melted to a clear liquid between 70 and 79°C. In contrast, samples which sublimed at 86°C, softened above 50°C but melted to a clear liquid in the range 82 to 85°C. Other characterization data include the following. Hydrolysis: 1.01 mol H_2/mol $Al(CH_2CMe_3)_2H$, 1.98 mol CMe_4/mol $Al(CH_2CMe_3)_2H$ (The compound is exceedingly sensitive to O_2 and H_2O, average of 11 analyses for both H_2 and CMe_4). Cryoscopic molecular weight, formula weight $Al(CH_2CMe_3)_2H$ 170.31 (molality based on monomeric species, obsd mol wt, association): 0.227, 433, 2.54; 0.109, 421, 2.47; 0.0871, 412, 2.42; 0.0590, 402, 2.36. The ^1H NMR spectra of benzene solutions are concentration dependent and details are

given in Table 2. IR (Nujol mull, cm^{-1}) 1770(s,br), 1360(s), 1260(w), 1225(s), 1200(sh), 1125(s), 1095(s), 1012(s), 995(s), 925(m), 910(m), 820(s), 760(m), 740(w), 705(m), 665(s), 560(w), 460(m), 400(m), 385(w), 330(m), 300(m).

Synthesis of $(Me_3CCH_2)_3Al\text{-}PPh_2H$. The reagents 1.327 g (5.52 mmol) of $Al(CH_2CMe_3)_3$ and 1.027 (5.52 mmol) of PPh_2H were combined in pentane. After the reaction mixture was stirred for several hours, the pentane was removed to leave the adduct as a colorless waxy-looking solid. $(Me_3CCH_2)_3Al\text{-}PPh_2H$: mp softens at 37°C, turns to an opaque liquid at 41.5 - 42.5°C, becomes transparent 44°C. ^1H NMR (d^6-benzene) δ 0.73(s, 6.0, CH_2), 1.23(s, 27.0, Me); 5.41(d, J_{P-H}=297 Hz, 1.0, P-H), 7.13, 7.53(m, 10.0, Ph-H). ^{31}P NMR (benzene) δ -31.22 (d, J_{H-P}=293 Hz). IR (Nujol mull, cm^{-1}) 3070(m), 3060(m), 2330(m), 2280(w), 1970(w), 1950(w), 1805(w), 1590(w), 1570(w), 1355(s), 1220(s), 1120(s), 1110(s), 1065(w), 1020(m), 1010(s), 995(s) 930(sh), 885(s), 815(s), 745(sh), 735(sh), 720(s), 685(s), 670(sh), 630(sh), 505(m), 470(m), 450(m), 425(w), 390(w), 330(m).

Synthesis of $(Me_3CCH_2)_2AlPPh_2$. This organoaluminum-phosphide was prepared by three methods. Method 1. The adduct $(Me_3CCH_2)_3Al\text{-}PPh_2H$ (0.44 g, 1.0 mmol) was heated at 180°C for 24 h to produce 0.97 mmol of CMe_4. The resulting solid was washed with 3 mL of pentane to yield 0.275 g $(Me_3CCH_2)_2AlPPh_2$ (0.776 mmol, 78% yield). Method 2. The reagents, 1.246 g (7.314 mmol) $Al(CH_2CMe_3)_2H$ and 1.362 g (7.314 mmol) PPh_2H were combined and then were heated at 105°C for 12 h to yield 7.13 mmol of H_2. The aluminum containing product was isolated as previously described to yield 2.17 g of $(Me_3CCH_2)_2AlPPh_2$ (6.12 mmol, 83.7% yield). Method 3. The reaction involved adding 0.895 g (4.00 mmol) of $KPPh_2$ to 0.995 g (3.99 mmol) of $Al(CH_2CMe_3)_2Br$ in 50 mL of hexane over 10 min. and stirring the mixture for 12 h. The

mixture was then filtered and the resulting solution was concentrated to 20 mL. Cooling of the resulting solution to -15°C produced large crystals of $(Me_3CCH_2)_2AlPPh_2$ (0.610 g, 1.72 mmol, 43.1% yield) which were isolated by filtration. Further crystallization raised the overall yield to 0.91 g (2.6 mmol, 75.2% yield). The characterization data for $(Me_3CCH_2)_2AlPPh_2$ prepared by the three methods were identical. $\underline{(Me_3CCH_2)_2AlPPh_2}$. Colorless, crystalline solid; mp loses crystallinity at 125°C, becomes opaque liquid at 180°C, transforms to clear liquid at 215°C. Anal. Calcd: C, 74.54; H, 9.12; P, 8.74; Al, 7.61. Found: C, 74.76; H, 7.13; P, 9.04; Al, 7.60. Cryoscopic molecular weight, formula weight $(Me_3CCH_2)_2AlPPh_2$ 354.22 (molality based on monomeric species, obsd mol wt, association): 0.133, 698, 1.97; 0.0691, 718, 2.03; 0.0357, 714, 2.02. ^1H NMR (d^6-benzene, 90 MHz) δ 0.98 (t, J=3.0Hz, 4.0, CH_2), 1.13(s, 18.0, Me), 7.13, 7.70(m, 10.0, Ph-H). ^1H NMR (d^6-benzene, 300 MHz) δ 0.96(t, J=3.0Hz, CH_2), 1.08(s, Me). ^{31}P NMR (benzene) δ-41.0(s). ^{13}C NMR (benzene) δ 30.66(t, J=9Hz, CH_2), 31.73(s, C), 34.99(s,Me). IR (Nujol mull, cm^{-1}) 3070(m), 3050(m), 1965(w), 1945(w), 1885(w), 1875(w), 1800(w), 1583(m), 1578(w), 1430(s), 1363(s), 1330(w), 1300(m), 1265(w), 1220(s), 1180(w), 1153(w), 1130(sh), 1115(m), 1090(m), 1020(m), 1010(m), 995(m), 930(w), 905(w), 838(w), 752(m), 740(s), 730(s), 685(s), 665(s), 640(m), 625(m) 568(w), 515(sh), 505(m), 458(m), 410(m), 330(w), 315(w), 285(m), 265(s).

$\underline{\text{Synthesis of } (Me_3CCH_2)_3Al\text{-}N(Me)H_2}$. Dry $MeNH_2$ (3.00 mmol, PVT) was combind with 0.497 g (2.07 mmol) of $Al(CH_2CMe_3)_3$ to produce an exothermic reaction. After excess amine was removed by vacuum distillation, a viscous liquid which slowly crystallized was obtained. Mass measurements indicated that 0.0645 g (2.08 mmol) of $NMeH_2$ reacted. The product quantitatively sublimed at 50°C. $\underline{(Me_3CCH_2)_3Al\text{-}N(Me)H_2}$. Colorless crystalline solid, mp

29-34°C. ^{1}H NMR (benzene) δ 0.20(s, 6.0, CH_2), 0.90(s, 2.0, NH_2), 1.20(s, 27.0, CMe), 1.48(s, 3.0, NMe). IR (Nujol mull, cm^{-1}) 3334(m), 3295(m), 3275(w), 1585(s), 1355(s), 1220(s), 1120(s), 1100(m), 1030(s), 995(s), 925(m), 905(w), 750(w), 715(w), 675(s), 645(s), 545(w), 470(m), 410(m), 390(m), 325(m).

Synthesis of $(Me_3CCH_2)_2AlN(Me)H$. Freshly sublimed $(Me_3CCH_2)_3Al\text{-}N(Me)H_2$ (0.5618 g, 2.061 mmol) was heated at 96°C for 10 h. After cooling, 2.07 mmol (PVT measurements) of CMe_4 was isolated by distillation. The aluminum containing product was isolated and purified by vacuum sublimation at 80°C (0.39 g, 2.0 mmol, 97% yield). $(Me_3CCH_2)_2AlN(Me)H$. Colorless solid, mp softens at 125°C, melts at 135-137°C. Anal. Calcd: C, 66.27; H, 13.17, N, 7.03; Al, 13.53. Found: C, 66.39; H, 13.08; N, 7.08; Al, 13.12. Cryoscopic molecular weight, formula weight $(Me_3CCH_2)_2AlN(Me)H$ 199.36 (molality based on monomeric species, obsd mol wt, association): 0.176, 392, 1.97; 0.0945, 385, 1.93; 0.0483, 406, 2.04. ^{1}H NMR (benzene) δ 0.31(s, 2.0, CH_2), 0.35(s, 2.0, CH_2), 0.75(q, J=6.6 Hz, 1.0, NH), 1.16(s, 18.0, C-Me), 2.03(d, J=6.6 Hz, 3.0, N-Me). IR (Nujol mull, cm^{-1}) 3320(m), 3180(w), 1355(s), 1220(s), 1135(m), 1120(s), 1095(m), 1060(m), 1025(s), 1010(sh), 930(m), 910(w), 810(s), 750(m), 740(m), 715(w), 660(s), 580(s), 515(s), 410(m), 360(w), 260(w). Raman (solid) 3320 cm^{-1}.

Results and Discussion

A series of neopentylaluminum compounds including $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2Br$, $Al(CH_2CMe_3)_2H$, $(Me_3CCH_2)_2AlPPh_2$ and $(Me_3CCH_2)_2AlN(Me)H$ as well as the adducts $(Me_3CCH_2)_3Al\text{-}N(Me)H_2$, $(Me_3CCH_2)_3Al\text{-}PPh_2H$ and $LiAl(CH_2CMe_3)_4$ have been prepared by very facile, high yield routes, have been easily purified and have been characterized. The preparative reactions were typical of those used to prepare the related trimethylsilylmethylaluminum compounds.[5,6] The characterization data for the compounds described herein include physical properties, elemental and/or group analyses, cryoscopic molecular weight measurements as well as infrared and NMR spectroscopic data. The compounds $Al(CH_2CMe_3)_3$ and $Al(CH_2CMe_3)_2H$ have been reported previously but either limited or no characterization data have been described. Trisneopentylaluminum[10] was originally prepared by reacting $AlMe_3$ with 2-methylpropene at 195-198°C and was characterized only by analysis and cryoscopic molecular weight measurements.[11] In contrast, the hydride[12] $Al(CH_2CMe_3)_2H$ has never been isolated but was believed to be one component of a product mixture which was obtained from the thermal decomposition at 110-140°C of $Al(CH_2CMe_3)_2(i\text{-}Bu)$, a compound prepared by mixing $Al(CH_2CMe_3)_3$ and $Al(i\text{-}Bu)_3$ in a 2:1 mole ratio. The product of this thermal decomposition was described as a mixture, 90 mol percent $Al(CH_2CMe_3)_2H$, 3 mol percent $Al(CH_2CMe_3)_3$ and 6 mole percent $Al(i\text{-}Bu)_3$.

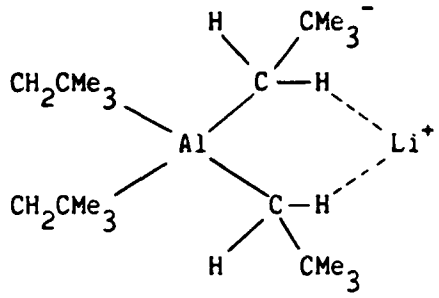
A significant feature of organogroup 13, especially aluminum, compounds relates to their tendency to associate and form dimers, trimers and/or higher oligomers.[1] A better understanding of the factors which influence the degree of association can be obtained by comparing the cryoscopic molecular weight measurements of these compounds (Table 1). At first, no simple, clear trend in the data is apparent. For compounds of the type AlR_3

and AlR_2H (electron deficient molecules), the neopentyl derivatives are less associated than the corresponding trimethylsilylmethyl analogs. In contrast, the neopentyl derivatives of the type R_2AlPPh_2 and AlR_2Br are more associated (electron precise species). These data suggest that a minimum of two factors related to steric and electronic effects influence the degree of association. Organoaluminum compounds with branched-chain alkyl substituents, such as $Al(CH_2CMe_3)_3$, $Al(i\text{-}Bu)_3$, $Al(t\text{-}Bu)_3$ and $Al(i\text{-}Pr)_3$, are observed to be monomeric[11] in benzene solution, whereas compounds without branched-chain substituents, such as $AlMe_3$,[13] $AlEt_3$[11] and $Al(n\text{-}Pr)_3$[11] are dimeric. Earlier workers suggested that the apparent bulk of the branched-chain substituent prevented association.[14] However, simple steric effects around aluminum cannot be a predominant factor. Aluminum derivatives with bulky branched-chain alkyl substituents form derivatives of the type $LiAlR_4$ ($R=CH_2CMe_3$, t-Bu[3] and i-Bu[14]). Thus, the AlR_3 derivatives have the available space for a fourth substituent. An alternate center for potential steric effects in AlR_3 species is the potentially bridging carbon atom, the α-carbon. This suggestion is consistent with the observation that $Al(CH_2SiMe_3)_3$ exists as a monomer-dimer equilibrium mixture,[4] whereas $Al(CH_2CMe_3)_3$ is a monomer.[11] The CH_2SiMe_3 substituent with its longer C-Si distance would have smaller steric effects at the potentially bridging carbon atom than the CH_2CMe_3 group with the shorter C-CMe_3 distance. An alternate or, possibly, additional reason for the lack of association of organoaluminum compounds with branched-chain alkyl groups is related to electronic effects. If the α-carbon atom has insufficient negative charge due to the electron withdrawing effects of the moieties bound to the α-carbon atoms (such as the CMe_3 group of CH_2CMe_3), electron deficient bridge bonding might have insufficient strength to overcome the loss of entropy for forming dimers

from monomers. It is well known that carbon is more electronegative than aluminum. Thus, the CMe_3 moiety should have a strong electron withdrawing effect, should weaken bridge bonding and consequently enhance the Lewis acidity at aluminum. It is, therefore, significant that the chemical shift of the methylene protons in $Al(CH_2CMe_3)_3$ is at a low field position, +0.56 ppm (benzene solution), and is consistent with the electron withdrawing nature of the CMe_3 group. For comparison, the chemical shift of the methylene protons in $Al(CH_2SiMe_3)_3$ is -0.22 ppm (toluene solution). The $SiMe_3$ group is reported to stabilize negative charge at the adjacent carbon atom.[16] Since the chemical shift of the protons on the α-carbon atom will be affected also by both the nature of the substituent as well as the degree of association, further comparisons are unwarranted. An alternative explanation for the lack of association of $Al(CH_2CMe_3)_3$, an intramolecular interaction between the aluminum and the hydrogen atoms on the Y-carbon atom with formation of a five-membered ring, was considered but ruled out on the basis of experimental observations. No infrared bands at frequencies, close to but below 3000 cm^{-1} were observed.

The Lewis acidity of the aluminum in $Al(CH_2CMe_3)_3$ has been demonstrated by its ability to react with Lewis bases and form adducts, an observation consistent with the proposed electron withdrawing character of the CMe_3 moiety and the CH_2CMe_3 substituent. The Lewis bases $CH_2CMe_3^-$, $N(Me)H_2$, PPh_2H and Et_2O form adducts. The formation of $LiAl(CH_2CMe_3)_4$ from $Al(CH_2CMe_3)_3$ and $LiCH_2CMe_3$ is supported by analytical and spectroscopic data. Even though the elemental analyses for carbon and hydrogen were low, the formation of 3.96 mol of CMe_4 per mol of $LiAl(CH_2CMe_3)_4$ hydrolyzed was clearly consistent with the formula. It is also noteworthy that the infrared spectrum of $LiAl(CH_2CMe_3)_4$ exhibits several intense bands at 2730

and 2710 cm^{-1}. These bands are most likely related to C-H stretching motions and suggest the presence of a C-H•••Li^+ interaction. The hydrogen involved in this C-H•••Li^+ (anion-cation) interaction should be the one with the highest negative charge, most likely the hydrogen atoms on the



α-carbon atoms of the anion. The group 15 bases $N(Me)H_2$ and PPh_2H also form simple adducts, $(Me_3CCH_2)_3Al\text{-}N(Me)H_2$ and $(Me_3CCH_2)_3Al\text{-}PPh_2H$. It is of interest that the amine adduct can be sublimed at 96°C. The phosphorus adduct has been confirmed by both ^1H and ^{31}P NMR. The P-H coupling constant increased from 218 Hz for pure PPh_2H[17] to 297 Hz for the adduct. The corresponding coupling constants[6] for $Me_3Al\text{-}PPh_2H$ and $(Me_3SiCH_2)_3Al\text{-}PPh_2H$ are 299 and 300 Hz, respectively. In contrast, $(Me_3CCH_2)_3Al\text{-}OEt_2$ is extensively dissociated at room temperature. An attempt was made to prepare ether-free $Al(CH_2CMe_3)_3$ by the Grignard route by using diethyl ether as solvent but the ether could not be quantitatively removed, even under azeotropic distillation with benzene, a technique used to prepare ether-free $InMe_3$.[18]

The compound $Al(CH_2CMe_3)_2H$ was prepared by reacting $Al(CH_2CMe_3)_3$ with $LiAlH_4$ in heptane heated with a 100°C oil bath. Our stoichiometric data suggest the following balanced equation for the preparative reaction. Earlier workers[19] used the same types of reagents to prepare Me_2AlH but

$$2Al(CH_2CMe_3)_3 + LiAlH_{4(s)} \xrightarrow[Reflux]{C_7H_{16}} 3Al(CH_2CMe_3)_2H + LiH_{(s)} \qquad (1)$$

different products and stoichiometry (equation 2) were observed. When

$$MMe_3 + LiAlH_4 \longrightarrow MMe_2H + LiAlMeH_3 \ (M=B, Al, Ga) \qquad (2)$$

3.67 g (15.3 mmol) of $Al(CH_2CMe_3)_3$ was reacted with 0.640 g (16.9 mmol) of $LiAlH_4$, 3.71 g (21.6 mmol) of purified $Al(CH_2CMe_3)_2H$ was isolated. If the reaction is based on equation 1, the percentage yield of product would be 95.2%. If equation 2 with the 1:1 $Al(CH_2CMe_3)_3/LiAlH_4$ stoichiometry were applicable, the percent yield would be 141%, an unreasonable value. In other experiments, the nonvolatile, insoluble residue, believed to be LiH and excess $LiAlH_4$, was hydrolyzed and the evolved H_2 was measured. These data support the formation of LiH, not $LiAl(CH_2CMe_3)H_3$.

Bis(neopentyl)aluminum hydride is a rare example of an aluminum hydride which melts above room temperature. The only other known example[6] is $Al(CH_2SiMe_3)_2H$. Cryoscopic molecular weight measurements indicate the existence of an equilibrium between dimeric and trimeric species with hydrogen bridge bonds. This equilibrium is also consistent with the ^1H NMR

$$2[Al(CH_2Me_3)_2H]_3 \rightleftharpoons 3[Al(CH_2CMe_3)_2H]_2 \qquad (3)$$

and IR spectral data. The three types of protons, CH_2, Me and Al-H, exhibit three sets of signals, two lines each. The intensity of each line of a set for a given type of proton varies with concentration as required by equation 3. The average equilibrium constant calculated from the NMR data is 0.22 M. Thus, the reactions interconverting dimer and trimer must be slow at the

operating temperature of the spectrometer. The presence of a broad, intense band at 1770 cm^{-1} is also consistent with structures with electron-deficient hydrogen bridge bonding.[6] The observation of a lower degree of association of $Al(CH_2CMe_3)_2H$ than $Al(CH_2SiMe_3)_2H$ is consistent with the electron-withdrawing properties of the neopentyl group. As the neopentyl group withdraws electron density from aluminum, the hydride becomes less basic and exhibits a weaker bridge bond and a reduced degree of association.

The aluminum phosphide $(Me_3CCH_2)_2AlPPh_2$ has been prepared by three synthetic routes, the elimination of hydrogen at 105°C from $Al(CH_2CMe_3)_2H$ and PPh_2H, the elimination of neopentane at 180°C from $Al(CH_2CMe_3)_3$ and PPh_2H, the elimination of KBr from $Al(CH_2CMe_3)_2Br$ and $KPPh_2$. Of these, the most convenient route involved the elimination of H_2 at moderate temperature. The product was readily isolated and purified in high yield. The concentration independent cryoscopic molecular weight data as well as ^1H, ^{31}P and ^{13}C NMR spectral data are consistent with the existence of only dimers in benzene solution. In comparison, $(Me_3SiCH_2)_2AlPPh_2$ exists as a monomer-dimer equilibrium mixture.[6] The observed higher degree of association of the neopentylaluminum derivative is consistent with the proposed electron withdrawing nature of the neopentyl group, and the higher Lewis acidity of the bis(neopentyl)aluminum moiety. Without the experimental data, one might have expected the neopentyl derivative with the more bulky substituent to be less associated than the corresponding trimethylsilylmethyl derivative. It is of significance that $(Me_3CCH_2)_2InPPh_2$ is also more associated than $(Me_3SiCH_2)_2InPPh_2$.[20]

The aluminum-nitrogen compound $(Me_3CCH_2)_2AlN(Me)H$ exists in benzene solution as a dimer as based on molecular weight measurements. The presence

of two different substituents on nitrogen introduces the possibility of cis-trans isomers. The spectroscopic data suggest the presence of only the cis isomer. The compound exhibits two CH_2 (neopentyl) resonances in the ^1H NMR spectrum and the coincidence of infrared and Raman bands at 3320 cm^{-1}, the region of the spectra expected for N-H stretching vibrations. It is of interest to note that $[(Me_3SiCH_2)_2AlN(Me)H]_2$ has been reported to exist as the trans isomer with only a single proton resonance for the methylene protons of CH_2SiMe_3.[4]

In summary, a comparison of data for the series of compounds AlR_3, AlR_2H, AlR_2Br, $R_2AlPPPh_2$ and $R_2AlN(Me)H$ demonstrate that neopentyl derivatives are less associated than trimethylsilylmethyl derivatives if they are electron deficient but more associated if they are electron precise. Presumably for electron deficient compounds withdrawal of electron density from the bridging unit is the dominant factor influencing the degree of association, whereas for electron precise compounds where there are plenty of electrons, the enhanced Lewis acidity of the aluminum is most important.

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Table 1

Degree of Association of Neopentyl- and Trimethylsilylmethylaluminum Compounds

Compound/R	(CH_2CMe_3)	(CH_2SiMe_3)
AlR_3	1	$1 \rightleftharpoons 2$
AlR_2H	$2 \rightleftharpoons 3$	3
AlR_2Br	$1 \rightleftharpoons 2$[a]	$1 \overset{a}{\rightleftharpoons} 2$
R_2AlPPh_2	2	$1 \rightleftharpoons 2$
$R_2AlN(Me)H$	2	2

a) At similar concentrations, the dimer is preferred for the neopentyl derivative whereas the monomer is preferred for the trimethylsilylmethyl derivative.

Table 2

90 MHz ^{1}H NMR Spectra of $Al(CH_2CMe_3)_2H$ in Benzene (ppm)

Concentration[a]	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(Al-H)$[c]	K^d(M)
0.090	0.63(0.60)[b], 0.70(0.40)	1.13, 1.17	3.13, 3.33	0.14
0.19	0.63(0.53), 0.70(0.40)	1.13, 1.15	3.17, 3.36	0.14
0.31	0.63(0.57), 0.70(0.43)	1.13, 1.15	3.13, 3.33	0.35
0.48	0.61(0.50), 0.68(0.50)	1.11, 1.13	3.10, 3.30	0.27
0.91	0.56(0.40), 0.63(0.60)	- , 1.13	3.08, 3.18	0.18
2.8	0.56(0.33), 0.63(0.66)	- , 1.13	3.08, 3.18	0.26

a) Concentration of monomer, M

b) Relative intensity of lines

c) Lines were very broad and overlapping

d) Equilibrium constant, K = $Dimer^3/Trimer^2$, Average 0.22M

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